

Interactive comment on “An improved ocean model of aluminium: the effects of circulation, sediment resuspension and biological incorporation” by M. M. P. van Hulten et al.

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Dear reviewer,

Your review contains a lot of useful points for improvement and we generally followed your suggestions. However, there are several points where we beg to differ. Several of them probably arise from badly chosen formulations in the manuscript that you reviewed (henceforth the Discussion Paper). Therefore we made an attempt to reformulate the text to avoid such misunderstandings. Finally, there remain some points at which our view differs from yours. We try to give arguments for our view in this rebuttal,

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part of which we also add to the paper. We believe that with revising the manuscript based on your and Van Beusekom's comments, these issues are for a large part resolved.

Certainly we did not try to rush through submission just to publish a repetition of a previous work. We carefully did the research and revised the manuscript to the point where we thought it was satisfactory for the reader and useful for our field. Nonetheless, improvements can be made. One of this is the title. After reading it time and again, we now understand that we may have put a red herring in the title concerning biological incorporation. You interpreted it that the incorporation should improve the model, and Van Beusekom possibly interpreted the title in such a way as if we tested the effect of biological incorporation of Al on the Si cycle. Neither was the intention. Hence the new title:

On the effects of circulation, sediment resuspension and biological incorporation in an ocean model of aluminium

1 “General comments.

What is different from van Hulten et al. (2013)? Reading through the manuscript and in particular the abstract it was very hard to distinguish what was really new and what was not a slightly modified version of simulation runs from the recently published work by the same authors (van Hulten et al., 2013). This was especially so when it come to upholding the promise of the title, "of an improved ocean model for Al", as it seems that many of the changes in the parameterizations resulted in a reduced ability to replicate the West Atlantic Al data set. It felt very much like a paper trying to sell negative results as an improvement! If a work like this is to be publishable it needs to set out its stall early about what and where the significant improvements were made and to provide an observational basis or link

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that support these improvements.”

There are significant improvements in the model compared with (Van Hulten et al., 2013). Firstly, the choice of a different circulation clearly shows a significant, positive effect on both $[\text{Si}_{\text{diss}}]$ and $[\text{Al}_{\text{diss}}]$. Nonetheless, the dynamics is only an underlying forcing field that not only has an impact on $[\text{Al}_{\text{diss}}]$ but the whole ocean biogeochemistry and hence this may require more analysis. We chose not to do that but rather (second point) put the attention to sediment resuspension – this is where a significant improvement is made. This resuspension and subsequent dissolution (dependent on bottom $[\text{Si}_{\text{diss}}]$) is very different from what we did in (Van Hulten et al., 2013). We have now made this more clear in our manuscript.

2 “Al incorporation into actively growing diatoms.

The authors should be aware that there are some studies that indicate that Al is not incorporated into the silicate structures of diatoms. Indeed other researchers from Groningen could previously not detect aluminium in diatom silicate for cultures spiked with aluminium (Vrieling et al., 1999). Indeed those authors suggested that the studies which indicated that aluminium is present in frustules of diatoms were cleaned by low-temperature ashing (Gehlen et al., 2002; van Bennekom et al., 1991; van Bennekom et al., 1989; Van Beusekom et al., 1997) and this procedure may not have removed aluminium associated with organic matter, while the HNO₃ oxidation method they employed did remove all the associated organic matter.”

Indeed some authors (e.g. Vrieling et al., 1999) present negative or inconclusive results on incorporation of Al into diatoms frustules. We made note of this in the introduction.

“Additionally recent work from groups based at Utrecht and NIOZ (Koning et al., 2007; Loucaides et al., 2012, 2010) have suggested that most of the Al found in
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diatom silicate in sediments is incorporated post burial. These papers indicate that the Al:Si ratio in living diatoms is most likely considerably lower than the estimates provided by the papers the model bases its assumptions on (Gehlen et al., 2002; van Bennekom et al., 1991; van Bennekom et al., 1989; Van Beusekom et al., 1997). Finally there is also related chemical evidence from work on the performance of concrete (Chappex and Scrivener, 2013), that aluminium is incorporated into silicate matrices over time. Thus it would significantly improve this work if the uncertainties of these assumptions were looked at in far more detail than they are at present.”

We have now included discussion on the subject of post-mortem incorporation. Most incorporation is indeed post burial and hence post-mortem. However, sedimentary processes are not the focus of this work and only matters are discussed that are of direct importance for the processes in the water column. What we aimed for here is to test the effect on $[\text{Al}_{\text{diss}}]$ by including biological incorporation using the upper limit of Al/Si (namely the ambient dissolved Al/Si). A study on sedimentary processes should contain discussion of these issues – we decided not to do this for the current work.

3 “Role of colloidal Al in Al cycling in the ocean.

Recent observational data from the Atlantic Ocean by Dammshäuser and colleagues (Dammshäuser and Croot, 2012; Dammshäuser et al., 2011; Dammshäuser et al., 2013) has indicated that colloidal Al that while it may be a small fraction of the dissolved Al pool, as seen in earlier works (Moran and Moore, 1989), it however plays an important role in controlling the removal rate and overall residence time of dissolved Al in the ocean. Their work strongly suggests that removal of dissolved Al is facilitated by complexation with colloidal and particulate organic carbon through a potentially reversible reaction in solution. Of course

sinking particles will transport this bound Al to greater depths and ultimately the sediments. Thus the Dammschäuser et al. work strongly suggests that any model of Al cycling in the ocean should incorporate an organic complexation model for the colloidal and particulate size fractions and that this is the main process by which dissolved Al is scavenged from the ocean and not direct biological incorporation into diatom frustules (see general comments above and below).”

At this stage, we do not think it is feasible to include more size fractions of Al or organic complexation in our model. Dammschäuser and Croot (2012) report a 0.2–3.4% colloidal fraction for Al. Even though the upper limit is not negligible, it is small nonetheless. They argue that the short residence times of dissolved Al in the ocean surface, as also reported by other studies, must mean one of two things:

- the removal of dissolved Al occurs mainly through direct adsorption; or
- the colloidal fraction is rapidly turned over.

In the first case, our model is reasonable in the sense that there is only one size fraction of particulate Al.

In the second case, our model is still reasonable in the following sense. The rapid turn-over of the colloidal fraction means that the transformation from colloidal Al to adsorbed Al is fast. In the case that it is much faster than the conversion from soluble Al to colloidal Al, this latter conversion determines $[Al_{diss}]$.¹ This means that in the model one may skip the colloidal fraction and model it as a single conversion from $[Al_{diss}]$ to $[Al_{ads}]$.

Although we did not consider Dammschäuser and Croot (2012) when writing the paper, it appears to be consistent with our previous conclusions that our empirical model of

¹Dammschäuser and Croot (2012) note that “the residence time in the soluble pool is controlled solely by transformation into the colloidal phase.” (p. 315)

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direct adsorption of Al_{diss} onto Si_{biog} is very reasonable, whether there is a colloidal fraction or not. We made a comment on this in the model description of the new version of the manuscript.

4 “Not all phytoplankton contain silicate.

Despite the recent finding (Baines et al., 2012) suggesting that some picoplankton also accumulate silicon in their cells it is clear that in oceanic regions where diatom productivity is low that the opal flux would be a poor proxy for the scavenging of dissolved Al. So how is Al scavenged in the oligotrophic North Atlantic under the Saharan dust plume?”

We agree that not all phytoplankton contain silicate. In our model only diatom frustules scavenge (and incorporate) Si, while nanophytoplankton do not. In the model description we note that PISCES has two phytoplankton types: nanophytoplankton and diatoms (P14546, L14–5). We added this for clarification in the model description.

Indeed, $[Si_{biog}]$ is very small in the oligotrophic North Atlantic Ocean (Van Hulst et al., 2013, Fig. 6), but $[Al_{diss}]$ is transported northwestwards by the gyre circulation (Van Hulst et al., 2013, Fig. 1). In the model the residence time of Al_{diss} in the oligotrophic part is generally less than 5 yr (Van Hulst et al., 2013, Fig. 18), so $[Al_{diss}]$ gets higher than in other regions. Removal by advection from this region is more important than scavenging (Van Hulst et al., 2013, Fig. 19).

5 “How well does the model replicate biogenic silicate concentrations?”

As the removal of dissolved aluminium is dependent on biogenic silica it would be extremely useful in the context of this work to see how well the model describes

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biogenic silica in the global ocean compared to observational data. As it appears at present that biogenic silica is scaled to primary productivity and may be potentially over represented in the oligotrophic gyres, i.e. do the nanophytoplankton also contain silicon? A better description of the basic model with regard to the primary productivity should be provided to facilitate examination of these aspects of the model.”

We give the necessary citations that show to what extent the model is correct. Figure 3 of Aumont and Bopp (2006) shows that primary production is small in the oligotrophic North Atlantic Ocean, consistent with measurement-induced biogenic silica export Sarmiento and Gruber (e.g. 2006, Color Plate 4). There are no data available for biogenic silica concentrations throughout the ocean. That is what we would need to validate our modelled $[Si_{bio}]$ on which Al depends.

Aumont and Bopp (2006) and the upcoming work by Aumont et al. provides a better description of the basic model with regard to primary productivity. It is outside the scope of this research on Al to do this here, so we did not extend our description of the underlying model or how well it performs.

6 “Aluminium concentrations in bottom waters: resuspension or diffusive flux?”

Resuspension of material from the sediments can be easily observed as nepheloid layers due to the changes in light scattering due to the presence of particles. These same particles may also scavenge dissolved aluminium from the water column despite the mixing event stirring in dissolved aluminium from the porewaters. There are almost no studies of dissolved Al in sediment porewaters, though one study in the Southern Ocean (Van Beusekom et al., 1997) does show smooth profiles that

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point to a diffusive flux of aluminium from the sediments to bottom waters. The diffusive flux is not considered in the present work and it may be more worthwhile to examine its influence on a global model in more detail despite the lack of data.”

We agree that the evidence for Si-dependent Al dissolution from sediments is inconclusive. Based on theoretical arguments and the observations, we have concluded that sediment resuspension and dissolution influenced by Si is the most consistent explanation so far.

The reason for putting more weight to the resuspension instead of diffusion, is the (indirect) evidence found for resuspension. This is based on observations that there appears to be an Al source from sediments where there is resuspension (e.g. around Grand Banks, Moran et al. 1991, associated with deep water formation or around seafloor elevations) but not a general source from sediments when there does not appear to be resuspension. This of course does not mean that there is no diffusion flux, but the observations link near-sediment Al elevations to regions of resuspension. Hence, this is tested with the model. Other possibilities should be tested too, but this is outside the scope of this paper.

Furthermore, the empirical model derived from resuspension and one derived from diffusion would be structurally identical. I.e., both processes result in a flux into the bottom model layer. Since it is not possible at the moment to model the underlying processes, the Al addition from the sediment is modelled as a flux. We now made clear in the manuscript that the model is based on resuspension and dissolution but is consistent with other processes like diffusion as well. The point is that there is a significant sediment source.

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7 “Technical comments.

P14541 line 17. As this is a central theme to the present work the authors should at the very least provide citations in support of this statement. See also the general comment on this above.”

Added citations in the first paragraph.

“P14541 line 20. Can the authors provide any evidence for the removal of Al by diatom production? There are a few studies (Moran and Moore, 1988a; Moran and Moore, 1988b; Moran and Moore, 1992; Ren et al., 2011) that have shown that it is part of the removal process but not the only mechanism occurring.”

Scavenging by $S_{i\text{biog}}$ is the main process of Al removal, as also you noted before. Therefore this process is part in all our model runs. In this paper we test the effect of biological incorporation, i.e. removal by diatom *production*, and find it to be small.

We have now added citations that provide evidence for the removal of Al by diatom production.

“P14541 line 22. Once again can the authors provide some references to back their claims here?”

Citations have now been added in first paragraph.

“P14542 line 7. What evidence does a modelling study (van Hulst et al., 2013) provide for this?”

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The evidence in Van Hulst et al. (2013) is that within the model configuration used, the distribution of Al_{diss} is worse when including subsurface dissolution. We reconsidered the value of this evidence and removed this citation. Instead, we note that most of the dust is refractory, i.e. only the outer few percent easily dissolve. We made this clear in the manuscript, and noted that there are no studies that really check whether Al from dust dissolves below the mixed layer.

“P14543 line 10. What other carrier phases are there? It seems biological silicate is the only one considered here. The earlier work (van Hulst et al., 2013) does mention the role of POM, $CaCO_3$ and lithogenic particles so why not here also?”

The earlier work explains why we only use biogenic silica and no other particulates. The previous work is more complete in its foundation. To make this clear, in the revised paper we refer more often to our previous paper for the fundamental assumptions.

“P14543 line 11. Along the west coast of North Africa, there is an apparently strong seasonal cycle in dissolved Al due to the deposition of Saharan dust (Helmert and van der Loeff, 1993; Hydes, 1983; Measures, 1995; Pohl et al., 2011; Rutgers van der Loeff et al., 1997), though this region is not a major zone for diatom productivity – how do the authors reconcile this with their current scheme in which Al removal is solely via uptake by, and the subsequent sinking of, diatoms?”

Actually, along the west coast of Africa there is significant diatom production compared to the rest of the tropical Atlantic Ocean, in both our model (Van Hulst et al., 2013, Fig. 6) and observations (e.g. Sarmiento and Gruber, 2006, Color Plate 4). Diatom production is small only compared to the Southern Ocean and northern North Pacific Ocean. Therefore, we do not make any comments on this in the paper.

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The seasonal cycle of Si is present in the model as silica concentrations are prognostically computed, and we also use a monthly dust deposition. This results in a small seasonal cycle of modelled $[Al_{diss}]$.

P14543 line 12. The Bruland and Lohan reference is a review chapter from a text book and contains no primary data on this process and therefore should be removed.

Okay, we removed the reference.

P14543 line 21. What is the Al:Si ratios at which the dissolution of silicate begins to be influenced by Al? See also the general comment on this above.

At this stage, this process has not been included.

P14544 line 27. What work are the authors referring to here? There is no citation listed and one can only assume then it is the unpublished Middag et al. work listed in the reference list. Thus there is no information provided so that the reader can check the author's claims regarding the high accuracy of this work.

You are quite right that only referring to Middag's unpublished work is not enough. However, we did expand on the accuracy claim in Van Hulst et al. (2013), as well as in the Discussion Paper on P14554, L11–16.

P14545 line 9. See the general comment regarding the evidence for the biological incorporation of Al into diatoms.

See our response to the general comment.

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P14545 line 17. What specifically are the 3 major changes from the earlier study (van Hulst et al., 2013)? As the circulation and biological incorporation are all considered in the earlier study, and the sediment source term was used in one of the reported sensitivity studies. As related to the general comment above it is hard to see what is significantly different about this work from the one published earlier this year.

This is explained in the beginning of our response. Furthermore, we know of no publication, except for this Discussion Paper, in which the effect of circulation on $[Al_{diss}]$ is investigated. Furthermore, global modelling of sediment resuspension and subsequent dissolution of Al has not been done before.

Although Han et al. (2008) included biological incorporation in their model, they did not study its impact explicitly. In our study this has been done by means of a sensitivity experiment.

P14548 line 14. The Lampitt (1985) work does not contain any information about Al chemistry in the sediments and thus it only has limited use here. There are works that directly address the chemistry of Al in the sediments (Koning et al., 2007; Loucaides et al., 2012; Loucaides et al., 2010). Additionally the work of Hwang et al. (2010) is appropriate here in terms of a related approach to estimate the resuspended flux of POC using particulate Al.

Quite right, but in our opinion the work of Koning et al. and Loucaides is of even less relevance for our work. While Koning and Loucaides are more mechanistic, our model connects better with Lampitt's work, since they discuss sediment resuspension. We have only added Hwang et al. (2010) to the citations at this place.

P14548 lines 21-25. These are the same equations as described previously for the published modelling study (Van Hulst et al., 2013).

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Yes, and important enough for the current work to repeat.

P14550 line 22. Presumably it is the pore water Si that is important here not the dissolved Si concentration in the water column? As the authors already mentioned in the text that there are no estimates of Al flux from resuspension then can they explain in more detail how dissolved Si controls dissolved Al concentrations in resuspended material?

It is a first-order assumption (P14567, L9). Since we lack the knowledge whether this is reasonable, it would be useful if this assumption were tested, but that is far outside the scope of this work. This reasoning has now been added to the text (in the Appendix).

P14558 line 19. There are data for dissolved Al in sediments (Mackin and Aller, 1986; Van Beusekom et al., 1997) and that could be used to calculate a diffusive flux to the water column in a manner typical to that used for iron and other nutrients. See the general comment about this above.

We would argue that despite this, the available data is too sparse to constrain a global ocean model in a mechanistic sense. We would note that even for iron, the sedimentary supply is only empirically formulated (Aumont and Bopp, 2006).

P14560 line 1. At what level is it statistically significant? Please provide some criteria here.

The criterium is given on P14556, L8–11.

P14560 line 19. Is there any experimental evidence to support the value used for the scavenging term in the present work?

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The value we used is within the range of reported values, but there is no consensus value of either k_d or κ (e.g. Gehlen et al., 2003; McAlister and Orians, 2011, for k_d ; κ is undetermined). Van Hulst et al. (2013) contains further discussion on k_d and κ .

P14561 line 11. This statement appears to support the findings of Vrieling et al. (1999) that Al is not incorporated into actively growing diatoms, see the general comment above. It may also simply reflect that the model requires more than two types of phytoplankton in order to simulate the processes more accurately.

It may well be necessary indeed to add another diatom functional class for realistically simulating the interaction between Si and Al. However, there are no observations available constraining such a more complex model.

P14562 lines 11/12, 16 and 19/20 Repetition - on the one hand and on the other hand...if ever there was a suspicion there was some dubious card trick going on, which hand am I meant to be watching?

This part was confusingly written. We tried to improve the reasoning here.

P14593 Figure A1. Is this calibrated transmissometer data?

Yes, it is.

8 Other changes.

We have made several additional changes to the document, namely:

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- Added citations that suggest there is only dust dissolution in the surface ocean.
- Replaced Fig. 2 with a more pleasant figure.
- Removed Figs. 3 and 4.
- Increased spin-up for all sensitivity simulations.
- Added five extra stations to West Atlantic GEOTRACES section, of which measurements were taken later to complete the transect.
- Redone statistics based on further spin-up and extra observations → statistical significance mostly not changed, but small changes in text were necessary. Only worsening of incorp+lower kd is not significant anymore.
- Added more recommendations to conclusion:
 - testing of other model configurations for incorporation
 - IF incorporation realistic, THEN test effect of Al on Si cycle
- Made mathematical notation more consistent.

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